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16. ABSTRACT

This document details the field validation of a test method for the sampling and analysis of formaldehyde emissions from stationary sources. Three potential source methods were evaluated.

Field testing of the methods were conducted at two different sites. At a formaldehyde manufacturing plant, where formaldehyde levels were high (>100 mg/m^3), samples were collected using the basic peroxide impinger method and the DNPH impinger method. At a formaldehyde user facility, where formaldehyde levels were low, samples were collected using the DNPH-coated cartridge method and the DNPH impinger method.

A statistical evaluation indicates that the DNPH impinger method is acceptable for determining both low and high concentrations of formaldehyde. Because of its range, this method is recommended as the reference method for determination of formaldehyde in source emissions.

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DEVELOPMENT AND VALIDATION OF A TEST METHOD FOR FORMALDEHYDE EMISSIONS

by

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FOREWARD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Formaldehyde is being evaluated for future emissions regulations because this compound is toxic and considered a cancer causing agent. Acceptable measurement methodology of these emissions from stationary sources is critical for proper assessment of the impact in the environment. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for quantification of formaldehyde emissions from stationary sources.

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ABSTRACT

Formaldehyde has been identified as a suspect carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. This document details the field validation of a test method for the sampling and analysis of formaldehyde emissions from stationary sources. Three potential source methods were evaluated. One method, the basic peroxide impinger/ion chromatography (IC) method is based upon the dissolution and oxidation of formaldehyde in the impinger reagent to form formate ion, which is measured by IC. The second method is a dinitrophenylhydrazine-coated (DNPH) cartridge/high performance liquid chromatography (HPLC) method, which is based on the reaction of formaldehyde with 2,4-DNPH and subsequent analysis of the hydrazone derivative by HPLC. The third method, the DNPH impinger/HPLC method extends the range of the cartridge method through the use of higher capacity DNPH impinger solutions.

Field testing of the methods were conducted at two different sites. At a formaldehyde manufacturing plant, where formaldehyde levels were high (> 100 mg/m^3), samples were collected using the basic peroxide impinger method and the DNPH impinger method. At a formaldehyde user facility, where formaldehyde levels were low, samples were collected using the DNPH-coated cartridge method and the DNPH impinger method.

A statistical evaluation indicates that the DNPH impinger method is acceptable for determining both low and high concentrations of formaldehyde. Because of its range, this method is recommended as the reference method for determination of formaldehyde in source emissions.

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SECTION 1
INTRODUCTION

Formaldehyde, a chemical that is widely used in a variety of industries, has been identified as a suspect carcinogen which may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. The U.S. Environmental Protection Agency (USEPA) has an ongoing program to evaluate and standardize source testing methods for hazardous pollutants, such as formaldehyde, in anticipation of future regulations.

The Research Triangle Institute (RTI) was contracted by the USEPA to perform an evaluation and field validation of a sampling and analysis method for formaldehyde emissions from stationary sources. In earlier studies, RTI evaluated and compared two formaldehyde methods in the laboratory to determine the potential acceptability of each for source measurements. The first of these, the basic peroxide impinger/ion chromatography (IC) method[1], is based upon the dissolution and oxidation of formaldehyde in the impinger reagent to form formate ion, which is measured by IC. The impinger reagent is a solution of 3% H_2O_2/0.025N NaOH. After sampling, the impinger solution is allowed to stand overnight before dilution and analysis in order for oxidation to be completed.

The second method evaluated in the laboratory is a DNPH-coated cartridge/high performance liquid chromatography (HPLC) method[2], which is based on the reaction of formaldehyde with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis of the hydrazone derivative by HPLC. The exposed cartridges are eluted in reversed direction with acetonitrile (ACN). The eluent is collected, made up to 5 mL with ACN, and analyzed by HPLC with no additional sample preparation.

The laboratory study (of these methods) revealed that they yielded similar results. The USEPA requested that the two methods be compared and validated under field conditions both at a formaldehyde user facility, where formaldehyde emissions were expected to be low, and at a formaldehyde manufacturing facility, where formaldehyde emissions were expected to be considerably higher. During preliminary experiments, it was discovered that the DNPH cartridges did not have sufficient capacity to sample the high levels of formaldehyde emitted from manufacturing facilities. Because of the need to sample

over a cycle of the plants operation, it is often not possible to reduce the flow rate sufficiently to obtain a representative sample. Therefore, a third method using higher capacity DNPH impinger solutions was evaluated.

Two three-day field tests were performed for the evaluation. The first field test was conducted at a formaldehyde manufacturing facility. Samples were collected using the peroxide impinger method and the DNPH impinger method. The second field test was performed at a furniture plant where a formaldehyde-containing glue was used in the veneering procedure. Samples were collected at this site using the DNPH-coated cartridge method and the DNPH impinger method.

This report summarizes the various activities performed in the study. The conclusions and recommendations are given in Section 2. Section 3 contains the experimental approach for the validation of each method. Results and a discussion for each method are presented in Section 4. Section 5 outlines the quality control procedures used in the study.

SECTION 2
CONCLUSIONS AND RECOMMENDATIONS

Three sampling/analysis methods were evaluated for use in the determination of formaldehyde in source emissions. A DNPH impinger/HPLC method and a basic peroxide impinger/IC method were field tested at a formaldehyde manufacturing site. The DNPH impinger/HPLC method and a DNPH-coated cartridge/HPLC method were field tested at a formaldehyde user site. The overall precision of each method was determined from the analytical results of simultaneously collected samples (4 samples per run and a total of 48 samples over a 3-day collection period).

The best precision was obtained with the DNPH-coated cartridge/HPLC method, which had a pooled standard deviation of 0.023 mg/m^3. The method was also the easiest to use, with no possibility of sample containers breaking or reagents spilling in the field. However, the capacity of the cartridge was exceeded quickly at the high concentrations (> 100 mg/m^3) of formaldehyde generally present at formaldehyde manufacturing facilities.

The DNPH impinger/HPLC method was tested at both the formaldehyde manufacturer site and the formaldehyde user site. A statistical evaluation indicates that this method is acceptable for determining both low and high concentration levels of formaldehyde.

Because of its poor detection limit, the basic peroxide impinger/IC method was found to be unsuitable for the determination of very low levels of formaldehyde (0.5 to 5 mg/m^3) such as those found at formaldehyde user sites. The method also yielded unacceptable results for the very high concentrations of formaldehyde (> 500 mg/m^3) sometimes found at formaldehyde manufacturing facilities, because the formaldehyde is not completely oxidized to formate ion. The method does show potential at intermediate levels (50-300 mg/m^3), and, because the reagents used are safer and easier to prepare in the field than those used for the DNPH impinger method, it is recommended that the oxidation reaction be studied further.

The major objective of the study was to develop and recommend a single method for sampling and analysis of formaldehyde over a wide range of concentrations (< 1 mg/m^3 to > 500 mg/m^3). The DNPH impinger/HPLC method meets this requirement and is therefore recommended as the reference method. However, in view of the excellent precision obtained for the DNPH-coated cartridge method and its ease of use, it is recommended that this method be approved as an alternate when low levels of formaldehyde are expected.

SECTION 3
EXPERIMENTAL APPROACH AND RESULTS

SITE SELECTION AND PRESURVEY

EPA requested that tests be performed at two sites, a formaldehyde manufacturing facility and a formaldehyde user facility, to determine the suitability of the methods for measuring both high and low concentrations of formaldehyde. Two field test sites were selected with the approval of the EPA Work•Assignment Manager, and a pre-test survey was conducted at each site.

During the pre-test survey of the formaldehyde user facility (a furniture manufacturing plant in western North Carolina), peroxide impinger samples and DNPH-coated cartridge samples were collected at two candidate sampling points within the plant. The first sampling point released formaldehyde emissions from a furniture gluing process and the second, emissions from a veneer press. The two sampling points yielded similar formaldehyde concentrations (2-6 mg/m^3). However, accessibility and working space considerations resulted in the selection of the veneer press sampling point for the field validation.

Collection of samples from the formaldehyde manufacturing plant required the assistance of an experienced stack sampler since samples had to be extracted from an approximately 50-foot stack. Since this requirement had not been anticipated, no samples could be collected during the presurvey. However, since the plant was located within 40 miles of RTI, it was decided that samples taken at the beginning of the field validation would be returned to RTI for analysis the same day so that any problems could be corrected before completion of the sampling.

FIELD TEST DESIGN

A three-day field test was conducted at each site. Each day, four (4) forty-five minute samples were collected in quadruplicate using the two methods judged appropriate for that site. Initially, peroxide impingers and DNPH-coated cartridges were used for sample collection at the manufacturing site.

However, the formaldehyde concentrations observed (500 mg/m^3 or greater) were much higher than anticipated and the capacity of the cartridges was exceeded quickly even at reduced sampling flow rates and times. Therefore, to increase capacity and allow collection of a representative sample, the DNPH-coated cartridges were replaced with impingers containing a more concentrated DNPH solution. At the formaldehyde user facility, where formaldehyde concentrations were much lower, both DNPH impingers and DNPH-coated cartridges were used for sample collection. The peroxide method was found to be unsuitable at these low levels due to the IC detection limit.

FIELD TESTING

The purpose of field testing was to determine the precision of each test method under field conditions and to intercompare the source concentrations measured by each method. Field tests of the three methods were conducted at two different sites. At the manufacturing site, (A), samples were collected from a formaldehyde production process using both the DNPH impinger method and the basic peroxide impinger method. At the users site, (B), samples were collected from a process in which an adhesive containing formaldehyde was used to bond wood or plastic veneer to a particle board or solid wood base. Both the DNPH impinger method and the DNPH-coated cartridge method were used at Site B. Samples were collected on 3 separate days at each site.

Technical Approach: Site A

Process Description --

Samples were collected from a formaldehyde production process at this site. In this process, formaldehyde gas from a reactor passes into the bottom of an absorber, through which water flows countercurrently to collect formaldehyde. The formaldehyde in water solution is removed from the bottom of the absorber as product. Formaldehyde which is not dissolved exits the top of the absorber and is recycled to the system. A portion of this absorber effluent gas was pumped to a sampling manifold during our testing.

Sampling Apparatus --

One end of a 3/8 inch OD plastic tube was placed in the top of the absorber stack and the other end was attached to the inlet of a Metal Bellows pump (MB-141) located on a platform near the base of the absorber. The pump outlet was attached to the inlet of a two-liter stainless steel canister with 1/4 inch OD Teflon tubing. The canister outlet was attached to a glass sampling manifold with 1/4 inch OD Teflon tubing. The purpose of the canister was to dampen pressure surges created by the manifold pump. The glass manifold was 1 1/4 inch OD and 3 1/2 feet long with 10 ports for sample train connection. The sampling ports were size 18/9 spherical ball joints. Size 18/9 spherical socket joints were located at the inlet and outlet of the manifold. The manifold outlet was attached to one end of a 3/8 inch ID Tygon tube with the other end placed in a flask containing water for observing excess manifold flow. A schematic of the sampling arrangement is shown in Figure 3-1.

Midget impingers for DNPH/acetonitrile sampling media were 25 mL capacity with size 12/5 ball joints. Each front impinger was connected to the manifold with a 1/4 inch OD Teflon tube with a 12/5 socket joint on one end and an 18/9 socket on the other end. A backup impinger was connected to the front impinger with a glass U-tube (12/5 sockets). The outlet of the backup impinger was attached to a charcoal tube with a 12/5 glass socket/rubber tubing adapter. The outlet of the charcoal tube was attached to an SKC Model 222 air sampling pump (50-200 cm^3/minute range) with Tygon tubing. Pump flow rates were calibrated in the laboratory prior to field sampling and a pump factor (cm^3/ count) was determined for each pump. The nominal flow rate for each pump was 75 cm^3/minute.

Midget impingers for hydrogen peroxide in water sampling media were 25 mL capacity with size 18/9 ball joints. The front impinger was connected to the sampling manifold with 1/4 inch OD Teflon tubing with 18/9 socket joints on both ends. A backup impinger was connected in series using a U-tube with 18/9 sockets. The outlet of the backup impinger was connected to a Dupont Model P4L sampling pump (500-4000 cm^3/minute range) with a size 18/9 socket and rubber tubing. The Dupont pumps were set to a nominal flow rate of 500 cm^3/ minute and calibrated in the laboratory prior to field testing.

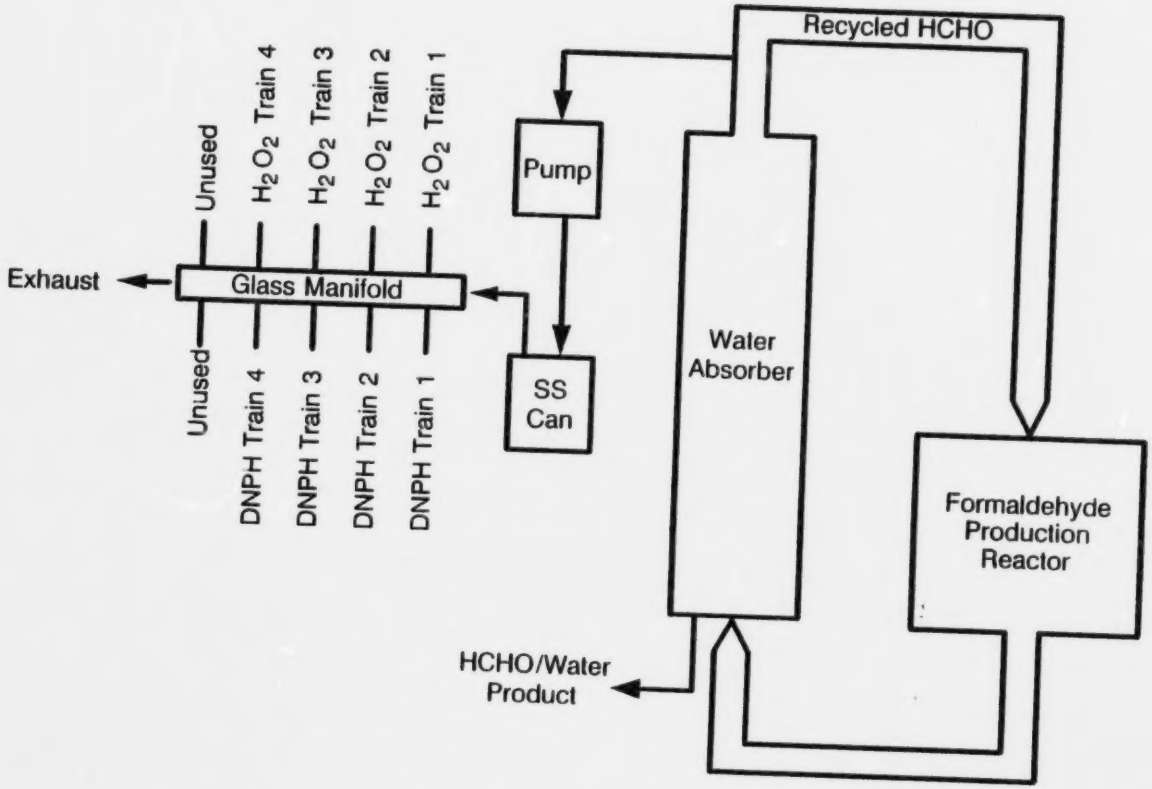

Figure 3-1. Site A field sampling schematic.

Sampling Media --

Saturated Stock DNPH Solution. The 2,4-DNPH used in the study was first purified by the method of Tejada, et al[2]. The purified crystals were placed in a 1-L glass bottle with a ground glass top. Approximately 50 mL of ACN was added to the bottle. The mixture was agitated gently and then allowed to stand overnight. ACN was added as necessary, taking care that a large excess of purified crystals remained in the bottom of the bottle. The saturated solution contains ~11 mg DNPH per mL at room temperature.

DNPH Impinger Solution. The DNPH impinger solution was prepared by diluting 25 mL of saturated DNPH stock solution to 100 mL with ACN and acidifying with 1.0 mL of 3.8 M $HClO_4$. Each impinger was charged with 20 mL of the solution.

Peroxide Impinger Solution. The basic peroxide impinger solution (3% H_2O_2/0.025 N NaOH) was prepared by adding 100 mL of 30% hydrogen peroxide to approximately 500 mL of deionized water in a 1-L volumetric flask. Then 25 mL of 1 N NaOH were added to the flask and the solution was made up to the mark with deionized water. Each impinger was charged with 20 mL of the solution.

Sampling Procedure --

Each set of DNPH/acetonitrile and H_2O_2 impingers was connected to the manifold and sampling pumps. The initial readings on the SKC pump counters were recorded. The manifold pump was started and the manifold was purged with source gas for 10 minutes prior to beginning sample collection. Sample pumps were started and sampling proceeded for 45 minutes. After the pumps were stopped, the final counter readings on the SKC pumps were recorded. Each impinger was sealed with parafilm, labelled, and stored in ice for return to the laboratory.

In some runs, an impinger series containing deionized water only was used at one manifold position. The purpose of these samples was to test for a formate background in the source gas which could interfere with the H_2O_2/IC measurement method for formaldehyde. Also, selected impingers were spiked with a known amount of derivative (for DNPH/acetonitrile method) or formate (for H_2O_2 method) to check analytical recovery.

Shown in Table 3-1 is a summary of the number and types of samples collected on each test day. During Run 3 on Day 1, the flow of source gas through the manifold was momentarily interrupted (possibly from a loss in electrical power to the manifold pump). The result was that water from the flask located at the manifold outlet was sucked into the manifold and the DNPH/acetonitrile impingers located in positions 1 and 2 were flooded. These samples were not analyzed. During Run 9 (on Day 3), the rubber tubing for the DNPH/acetonitrile sample pump at position 1 became disconnected from the charcoal tube. Since ambient air was sampled with the pump for an unknown period of time, the actual source gas sample volume could not be recovered and this sample was discarded.

Technical Approach: Site B

Process Description --

Samples were collected at this site from a process involving bonding of wood or plastic veneer to a particle board or solid wood base. In this process, an adhesive which contains formaldehyde is applied to one side of a veneer sheet. The sheet is placed on top of a piece of particle board or solid wood and the piece is transferred into a heated press. The press is activated, the veneer sheet is bonded to the base, and the piece is then conveyed out of the press. The gases released during the heating process, including formaldehyde, are exhausted through the roof of the building by a large fume hood located above the press. Exhaust gas from the duct connecting the fume hood to a blower was pumped to a sampling manifold during our testing.

Sampling Apparatus --

The apparatus used for transferring source gas to the sampling manifold at Site B was identical to that used at Site A except that 1/4 inch OD Teflon tubing was used as a transfer line from the exhaust duct to the manifold. A schematic of the sampling arrangement is shown in Figure 3-2.

Sampling with DNPH/acetonitrile was performed as described earlier for Site A except that the nominal pump flow rate was 200 cm^3/minute.

TABLE 3-1. SITE A FIELD SAMPLING SCHEME

	Day 1 (9-2-88)															
	Run 1				Run 2				Run 3				Run 4			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
DNPH/ACN Pair:	X	X	X	X	X[a]	X	X[a]	X	X	X	X	X	X		X	X
H_2O_2/H_2O Pair:	X	X	X		X	X	X		X	X	X		X	X		
H_2O only Pair:				X				X				X			X	X

	Day 2 (10-14-88)															
	Run 5				Run 6				Run 7				Run 8			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
DNPH/ACN Pair:	X	X	X	X	X[a]	X	X	X	X	X	X	X	X	X	X	X[a]
H_2O_2/H_2O Pair:	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
H_2O only Pair:																

	Day 3 (10-26-88)															
	Run 9				Run 10				Run 11				Run 12			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
DNPH/ACN Pair:	X	X	X[a]	X	X	X	X	X	X	X	X	X[a]	X	X	X	X
H_2O_2/H_2O Pair:		X	X	X	X		X	X	X[b]	X		X	X[b]	X	X	
H_2O only Pair:	X					X					X					X

a Derivative spike of front impinger.
b Formate spike of front impinger.

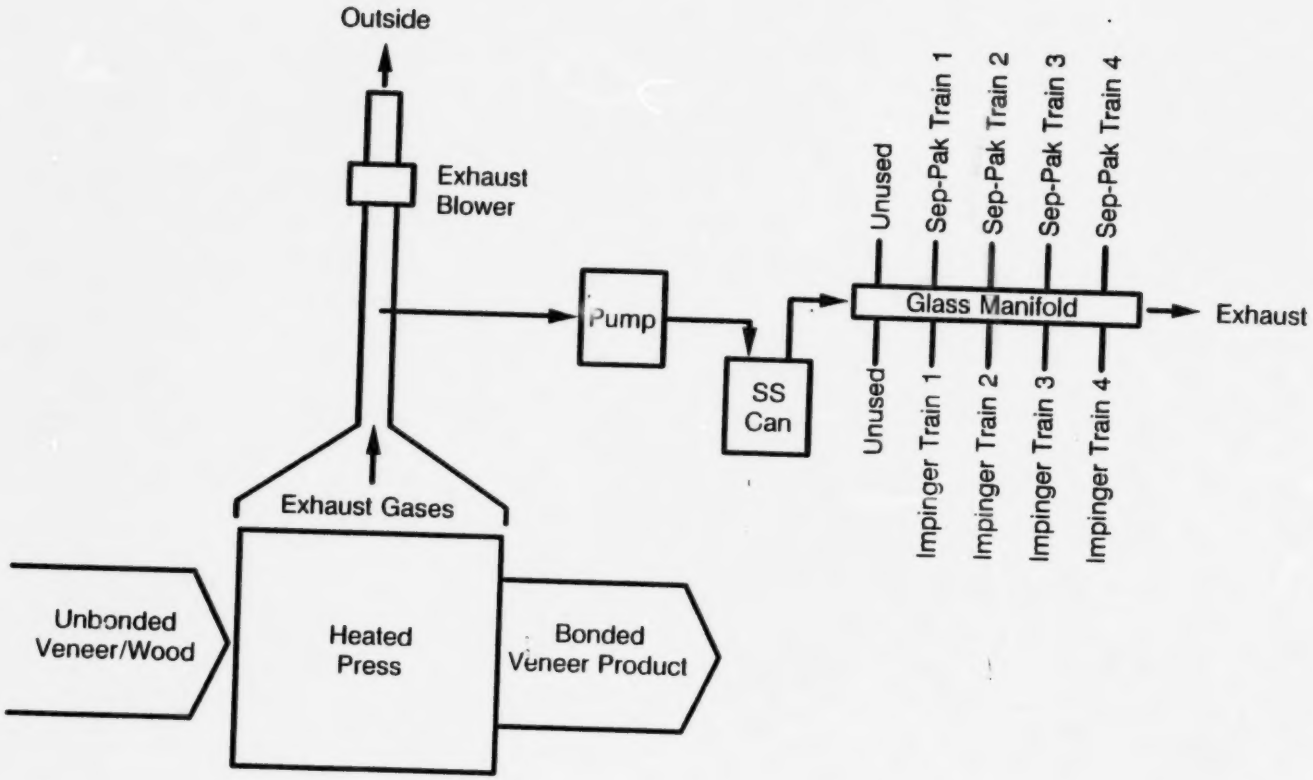

Figure 3-2. Site B field sampling schematic.

A third method was tested at this site which involved sampling onto Sep-Pak cartridges coated with DNPH. The Sep-Pak cartridge consisted of a polyethylene body packed with a silica support which had been surface-coated with 1.9 mg of DNPH in the laboratory. Sep-Paks were connected to the sampling manifold with a socket joint/Teflon tubing adapter. When a back-up Sep-Pak was used, it was connected to the front cartridge with a short length of 1/4 inch OD Teflon tubing. The Sep-Pak outlet was connected to an SKC Model 222 sampling pump with Tygon tubing. The pumps were calibrated at a nominal flow rate of 100 cm^3/minute in the laboratory.

Sampling Media --

DNPH Impinger Solution. The DNPH impinger solution was identical to that used at site A.

Coated Cartridges. The Sep-Pak cartridges were coated according to the method of Tejada, et al[2]. The coating solution was prepared by diluting 30 mL saturated DNPH solution to 1000 mL with ACN and acidifying with 1 mL concentrated HCl. The short end of each cartridge was connected to a 10-mL disposable plastic syringe and the syringe was placed in a rack. Using a repetitive pipet, 10 mL ACN were added to each syringe and the liquid was allowed to drain, by gravity, into a waste container. When the ACN rinse solution had completely drained, 7 mL of the coating reagent were pipetted into each syringe. When the coating solution had completely drained, the excess liquid at the outlet of each cartridge was wicked with a clean tissue. The cartridges were dried by passing nitrogen through each at a flow rate of 300-400 mL/min for 15 minutes. The cartridges were capped using luer plugs and placed into individual glass tubes until they were used for sampling.

Sampling Procedure --

Prior to starting the manifold pump, each set of DNPH/acetonitrile impingers and Sep-Pak cartridges was connected to the manifold and sampling pumps. The initial SKC pump counter readings were recorded and the manifold was purged for 10 minutes with source gas. The sample pumps were then started and sampling continued for 60 minutes. After stopping the pumps, the final pump counter readings were recorded, each impinger was sealed with parafilm

and labelled, and each Sep-Pak cartridge was sealed with luer plugs and placed in a labelled screw cap glass vial. Both impingers and Sep-Paks were stored on ice for return to the laboratory.

Shown in Table 3-2 is a summary of the number and types of samples collected on each test day. Selected impingers were spiked with derivative in the laboratory prior to field sampling to enable testing of analytical recovery. These spiked samples are identified in the table. Backup impingers and Sep-Paks were used for all samples collected on Day 1, but only one sample in each run on Days 2 and 3 consisted of two devices in series. This arrangement was based on results of analyzing Day 1 samples in which no breakthrough was observed.

SAMPLE ANALYSIS

Sample Preparation

DNPH Impingers --

Samples were collected in quadruplicate using pairs of midget impingers in series, each containing 20 mL of the acidified DNPH collection solution. For one pair of impingers from each quadruplicate set of samples, the front and back impinger samples were analyzed separately to ensure that there was no significant breakthrough. Each impinger sample was quantitatively transferred to a 25-mL volumetric flask and diluted to the mark using acetonitrile. For the remaining impinger pairs, the contents of the impingers were combined and diluted to a known volume using acetonitrile. Additional dilutions were performed as necessary to bring the samples into the range of the calibration standards. Samples were analyzed by direct injection into the HPLC.

DNPH-Coated Cartridges --

Samples were collected in quadruplicate using pairs of DNPH-coated cartridges connected in series. Each cartridge sample was eluted , according to the method of Tejada[2], in reversed direction by gravity feed using 6 mL ACN. The eluate was collected in a 5-mL volumetric flask and made up to the mark with ACN. The samples were analyzed by direct injection into the HPLC.

TABLE 3-2. SITE B FIELD SAMPLING SCHEME

	Day 1 (11-10-88)															
	Run 1				Run 2				Run 3				Run 4			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Impinger:	X	X[a]	X	X	X	X	X	X	X[a]	X	X	X	X	X	X	X
Sep-Pak:	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

	Day 2 (12-1-88)															
	Run 5				Run 6				Run 7				Run 8			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Impinger:	X[b]	X	X	X	X[b]	X	X	X[a]	X[b]	X	X	X	X[b]	X	X[a]	X
Sep-Pak:	X[b]	X	X	X	X[b]	X	X	X	X[b]	X	X	X	X[b]	X	X	X

	Day 3 (12-2-88)															
	Run 9				Run 10				Run 11				Run 12			
Position:	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Impinger:	X[b]	X	X	X	X[a,b]	X	X	X	X[b]	X	X	X	X[b]	X[a]	X	X
Sep-Pak:	X	X	X	X	X[b]	X	X	X	X[b]	X	X	X	X[b]	X	X	X

[a] Derivative spike of front impinger.
[b] A back-up impinger or Sep-Pak was used. (Note: back-up impingers and Sep-Paks were used for all runs on Day 1).

Peroxide Impingers --

Samples were collected in quadruplicate using pairs of midget impingers connected in series, each containing 20 mL of 3% H_2O_2/0.025 N NaOH. The samples were allowed to stand overnight prior to preparation for analysis. For one pair of impingers for each quadruplicate set of samples, the front and back impinger samples were analyzed separately to ensure that there was no significant breakthrough. Each front impinger sample was quantitatively transferred to a 50-mL volumetric flask and brought to volume using the basic peroxide impinger solution. The back impinger was transferred to a 25-mL volumetric flask and brought to volume with impinger solution. An aliquot of each sample was diluted 5-fold using deionized water and analyzed by direct injection into the ion chromatograph. For each remaining impinger pair, the samples were combined in a 50-mL volumetric flask and diluted to the mark using impinger solution. These samples were also diluted 5-fold using deionized water before
analysis by IC.

Calibration

High Performance Liquid Chromatography --

The formaldehyde DNPH derivative for the calibration standards was prepared by the method of Tejada[2], et al, as follows. To approximately 10 mL of 2N HCl in a 50-mL beaker were added 7.8 mL saturated DNPH in ACN solution and 40μL formaldehyde. The bright yellow precipitate was collected on a 9-cm Whatman No. 1 filter and washed with 50 mL 2N HCl and 30 mL deionized water. The filter containing the precipitate was folded and placed back into the original beaker, covered with a clean filter, and allowed to air dry.

A stock solution of the formaldehyde DNPH derivative was prepared by transferring an accurately weighed quantity of the derivative into a volumetric flask and filling to the mark with acetonitrile. A series of calibration standards were prepared by dilution of the stock solution using acetonitrile. At least three calibration standards, bracketing the concentration range of the samples, were used to prepare a calibration curve.

Ion Chromatography --

A stock solution of 1000 mg formate ion per liter was prepared by dissolving 1.5110 g reagent grade sodium formate in deionized water. Calibration standards were prepared by appropriate dilutions of the stock solution. Hydrogen peroxide and sodium hydroxide were added to each standard so that the resulting matrix was the same as that for the diluted samples (i.e., 0.6% H_2O_2/0.005N NaOH). At least three calibration standards, bracketing the concentration range of the samples, were used to prepare a calibration curve.

Instrumentation

High Performance Liquid Chromatography --

Analyses were performed using a Varian 5000 liquid chromatograph equipped with a 20-μL sample loop and a Varian UV-50 variable wavelength detector set at 365 nm. A Zorbax-ODS column was used (25 cm x 4.6 mm ID) for the HPLC separation. Isocratic conditions were maintained with 65% acetonitrile and 35% water at a flow rate of 1 mL/min. Quantitation by peak area integration was performed using a Shimadzu C-R3A Chromatopac.

Ion Chromatography --

A Dionex Model 14 ion chromatograph equipped with an 800-μL sample loop and a conductivity detector was used for analysis of the peroxide impinger samples. Ion chromatographic separation was achieved using Dionex AG3 and AS3 guard and separator columns, respectively, and a Dionex anion micromembrane suppressor column. The eluant used was 0.003 N $NaHCO_3$/0.0024N Na_2CO_3 at a flow rate of 2.3 mL/min. Quantitation by peak area integration was accomplished with a Dynamic Solutions Maxima chromatography workstation.

SECTION 4
RESULTS AND DISCUSSION

SITE A: FORMALDEHYDE MANUFACTURING FACILITY

Samples collected at the formaldehyde manufacturing site using both the DNPH impinger method and the basic peroxide impinger method were returned to the RTI laboratory for analysis by HPLC and IC, respectively. The analytical results are presented and discussed in this section.

Analytical Results: DNPH Impinger/HPLC Method

The results from the HPLC analysis of the DNPH impinger samples are presented in Table 4-1. The data from Run 3 are questionable because a brief power failure led to a back-up of water in the sampling manifold. For samples marked with an asterisk, the front impinger was spiked with a known quantity of the formaldehyde DNPH derivative to check the analytical recovery. The spiking concentration has been subtracted from the result given in the table. Spiked samples and samples from Run 3 were not included in the statistical analysis of the data. The means and standard deviations are also given in the table. The standard deviation appears to vary in proportion to the mean (i.e, the highest values for the standard deviation are associated with the highest values for the mean and, similarly, the lowest values of the standard deviation are associated with the lowest values for the mean). To determine if this apparent relationship between the standard deviation and the mean is true, the standard deviation was modeled as a function of the mean using linear regression as follows:

$$\text{std. dev.} = a + b^{*}\text{mean}$$

where a is the intercept and b is the slope. If the standard deviation does increase as the mean increases, then the slope of the resulting line will be significantly different from zero. If the level of the mean has no effect on the standard deviation (i.e., if the standard deviations are homogeneous), then the slope will be zero. A t-test is used to determine if the slope is significantly different from zero with a critical value of 2.262 at the 95%

TABLE 4-1. SITE A: FORMALDEHYDE MANUFACTURING FACILITY - DNPH IMPINGER RESULTS

Formaldehyde Concentration, mg/cubic m

Run No.	Manifold Position 1	2	3	4	Mean	Std. Dev.	%RSD
1	267.2	269.3	262.7	250.1	262.3	8.6	3.3
2	290.4*	315.8	271.2*	269.8	292.8	32.5	11.1
3	-----	-----	269.0	204.4	236.7	45.7	19.3
4	296.9	-----	308.1	266.2	290.4	21.7	7.5
5	41.6	46.9	48.1	47.9	46.1	3.1	6.6
6	77.3*	56.8	58.1	58.9	57.9	1.1	1.9
7	52.4	64.0	66.4	64.0	61.7	6.3	10.2
8	70.4	60.0	78.5	16.8*	69.6	9.3	13.4
9	-----	718.7	712.9*	708.9	713.8	6.9	1.0
10	623.4	730.0	735.3	748.0	709.2	57.7	8.1
11	669.2	772.6	774.7	760.1*	738.8	60.3	8.2
12	664.5	785.0	812.9	782.5	761.2	65.9	8.7

* Spiked samples. Spiking concentration has been subtracted from the result given in the table.

confidence level with 9 degrees of freedom. For DNPH impinger data, the t-value is 3.83 indicating that the slope is significantly different from zero and the standard deviation did vary with the mean. This variation in the standard deviation of the mean is possibly due to variation in the source itself.

Analytical Results: Basic Peroxide Impinger/IC Method

The results from the IC analysis of the basic peroxide impinger samples for the first two days of sampling (8 runs) are presented in Table 4-2. For each of the first four runs, a set of impingers containing deionized water was used to check for the presence of formate ion which would result in a positive interference in the IC analysis. Since only a very small amount of formate (~1 mg/m^3 as formaldehyde) was observed in the stack gas, the water impingers were not used in the next four runs. Again, the data from Run 3 are questionable. Statistical treatment of the peroxide impinger samples using the results of seven runs could not confirm a level dependence, such as that found for the DNPH impinger samples, due to the extensive data scatter.

The data from the last day of sampling (Runs 9 through 12) are presented in Table 4-3. On this day, the formaldehyde concentration in the stack gas exceeded 500 mg/m^3. Again, a set of impingers containing deionized water was included in each run to check for the presence of formate ion. The concentrations of formate ion (as formaldehyde) ranged from 1 to 17 mg/m^3, which is not judged to be significant at the formaldehyde levels observed.

The front impingers for samples 11-1 and 12-2 were spiked with accurately weighed quantities of sodium formate prior to sample collection to check the analytical recovery. The spiking concentration has been subtracted from the result given in the table.

Examination of the data reveals that, at formaldehyde concentrations greater than 600 mg/m^3, oxidation of the formaldehyde to formate ion in the peroxide impingers appears to be incomplete. For samples 9-3, 10-4, 11-2, and 12-3, the front and back impinger solutions were analyzed separately to test for sample breakthrough. The sample from each impinger (20 mL) was quantitatively transferred to a 50 mL volumetric flask and made up to the mark with fresh impinger solution (3% H_2O_2/0.025 N NaOH). For the remaining samples, the front and back impingers were combined (40 mL) in a 50 mL volumetric flask

TABLE 4-2. SITE A: FORMALDEHYDE MANUFACTURING FACILITY - BASIC PEROXIDE IMPINGER RESULTS RUNS 1-8

Formaldehyde Concentration, mg/cubic m

Run No.	Manifold Position 1	2	3	4	Mean	Std. Dev.	%RSD
1	276.8	286.8	296.1	(1.2)	286.6	9.7	3.4
2	283.0	304.3	261.4	(1.0)	282.9	21.5	7.6
3	261.6	338.4	250.0	(0.9)	283.3	48.0	17.0
4	253.3	326.0	(1.1)	(1.1)	289.7	51.4	17.7
5	54.4	58.9	62.0	58.9	58.6	3.1	5.3
6	69.4	79.0	70.2	78.1	74.2	5.1	6.8
7	54.5	-----	92.9	87.4	78.3	20.8	26.5
8	105.8	101.4	108.3	118.2	108.4	7.1	6.6

TABLE 4-3. SITE A: FORMALDEHYDE MANUFACTURING FACILITY - BASIC PEROXIDE IMPINGER RESULTS RUNS 9-12

	Formaldehyde Conc, mg/cubic m
Run 9	
9-1	(0.9)[a]
9-2	767.2 + 9.2[b]
9-3	472.4 (910.7)[c]
9-4	466.2
Run 10	
10-1	504.6
10-2	(10.3)[a]
10-3	793.3 + 7.6[b]
10-4	446.8 (983.1)[c]
Run 11	
11-1	490.8
11-2	469.8 (684.6)[c]
11-3	(10.5)[a]
11-4	793.6 + 9.8[b]
Run 12	
12-1	865.2 + 8.5[b]
12-2	482.4
12-3	483.1 (745.6)[c]
12-4	(17.5)[a]

[a] Formate, as formaldehyde, collected in deionized water impinger.
[b] Front impinger and back impinger (analyzed separately).
[c] Reanalysis after addition of fresh impinger solution.

and made up to the mark with impinger solution. All samples were diluted 5-fold with deionized water prior to analysis. In each case, the front impinger from the pair that were analyzed separately yielded a higher formaldehyde concentration than the remaining samples from the same run. Since a greater amount of fresh impinger solution was added to the front impinger than to the combined impingers (~30 mL instead of ~10 mL), there was more peroxide available for the oxidation of unreacted formaldehyde to formate ion. To test this hypothesis, fresh impinger solution was added to aliquots of samples 9-3, 10-4, 11-2, and 12-3. The analytical results for these samples are given in parentheses in Table 4-2. In each case, a significant increase in formaldehyde concentration was observed. Note that the results for samples 9-3 and 10-4 exceed the concentrations found using the DNPH impinger/HPLC method. The formaldehyde to formate ion oxidation reaction needs further study.

Methods Comparison: DNPH Impinger/HPLC and Basic Peroxide Impinger/IC

The DNPH Impinger/HPLC and Basic Peroxide Impinger/IC data were evaluated to determine if the two methods were statistically equivalent at the 95% confidence level. Because of the range of the means and the character of the DNPH impinger variances (i.e., the standard deviations increase in proportion with the means), the Site A data sets could be compared only after a log transformation. This transformation is performed to stabilize the variances (i.e., the variance should be the same no matter what the level of the mean). To determine if the variances of the transformed data were homogeneous, the data sets were tested using the Bartlett test[3]. The Chi Squared statistic is used in the test with a critical value of 18.3 at the 95% confidence level for the DNPH data. The calculated Chi Squared value for the DNPH data set was 7.95. For the peroxide data set, the critical value was 12.6 and the calculated value was 12.4. The transformation had, in fact, resulted in homogeneous variances. Therefore, standard deviations could be calculated for the data sets as a whole that were more representative of the data than values calculated from any run. The pooled standard deviations for the transformed DNPH and peroxide data sets were calculated to be 0.070 and 0.102, respectively. (These values correspond to coefficients of variation 7 and 11 percent.) Following this, the means of the transformed data were compared with each

other using analysis of variance for a two-way classification as shown in Table 4-4. The calculated F-statistic for the method effect, 7.25, exceeded the critical value, $F_{1,6} = 5.99$, indicating that the data sets (i.e., the methods) were significantly different at the 95% confidence level. The mean of this difference in the transformed values, 0.171 ± 0.059, corresponds to a difference of 19 percent in the measured values on the original scale, with the peroxide impingers yielding higher values than the DNPH impingers. There is no obvious explanation for this difference. It is interesting to note, however, that the difference ranges from -0.2 to +19.7 percent for the higher levels, i.e., Runs 1 - 4, and from +26.9 to +55.8 percent for the lower levels, i.e., Runs 5 - 8. If the problem was incomplete reaction of the DNPH with the formaldehyde, then one would expect a greater difference at the high concentration and not at the low concentration. Also, no significant breakthrough was measured and, as noted later in Section 5, DNPH-formaldehyde derivative spiked into select impingers showed good recovery. A likely explanation for the difference is the presence of an interferent formed by reaction with peroxide; as noted, there is no significant formate in the source stream.

SITE B: FORMALDEHYDE USER SITE

Samples collected at the formaldehyde user site using both the DNPH impinger method and the DNPH-coated cartridge method were returned to the RTI laboratory for analysis by HPLC. The analytical results are presented and discussed in this section.

Analytical Results: DNPH Impinger/HPLC Method

The results from the HPLC analysis of the DNPH impinger samples are presented in Table 4-5. For samples marked with an asterisk, the front impinger was spiked with a known quantity of the formaldehyde-DNPH derivative to check for analytical recovery. The spiking concentration has been subtracted from the result given in the table. Spiked samples were not included in the calculations of mean, standard deviation, and relative standard deviation. The precision of the DNPH method is acceptable with an average RSD of 5.7% and a range of 0.7 to 15.1%. In some cases (Runs 1, 9, 11, and 12), the formaldehyde concentration found in the first sample (which was always collected from

TABLE 4-4. FORMALDEHYDE SITE A DATA

LOG-TRANSFORMED VALUES

TWO-WAY ANOVA

Run No.	DNPH Impingers	Peroxide Impingers
1	5.569	5.658
2	5.676	5.643
4	5.669	5.661
5	3.830	4.069
6	4.059	4.305
7	4.118	4.333
8	4.237	4.684

$\bar{x}$ = 4.822

s^2 = 0.54129

Analyses of Variance

Source	Degrees Freedom	Sums of Squares	Mean Squares	F-value
METHOD	1	0.102	0.102	7.25*
RUN	6	7.392	1.232	87.62
ERROR	6	0.08437	0.01406	
TOTAL	13	7.578		

$F_{1,6}$ for 95% confidence level 5.99
Method differences are significant

* Significant at 95% confidence level

TABLE 4-5. SITE B: FORMALDEHYDE USER FACILITY - DNPH IMPINGER RESULTS

Formaldehyde Concentration, mg/cubic m

Run No.	Manifold Position 1	2	3	4	Mean	Std. Dev.	%RSD
1	0.667	0.723*	0.755	0.782	0.735	0.060	8.2
2	1.867	1.819	1.942	1.898	1.882	0.052	2.8
3	1.476*	1.579	1.598	1.507	1.561	0.048	3.1
4	0.777	0.772	0.788	0.716	0.763	0.032	4.2
5	0.843	0.728	0.835	0.897	0.826	0.071	8.6
6	1.325	1.286	1.236	1.293*	1.282	0.045	3.5
7	0.821	0.808	0.833	0.857	0.830	0.021	2.5
8	0.789	0.790	0.828*	0.780	0.786	0.006	0.8
9	0.586	0.684	0.642	0.667	0.645	0.043	6.6
10	0.963*	1.126	1.236	1.201	1.188	0.056	4.7
11	0.740	0.894	0.854	0.840	0.832	0.065	7.9
12	0.625	0.864*	0.811	0.834	0.756	0.115	15.2

* Spiked samples. Spiking concentration has been subtracted from the result given in the table.

the same position in the manifold) is significantly lower than the concentrations found in the remaining samples. No explanation for this observation has been found.

As with the Site A data, the data were tested to determine if the standard deviation increased as the mean increased. Linear regression of the standard deviation on the mean yielded a calculated t-value of 0.747 which is less than the critical value of 2.228 for 10 degrees of freedom and the 95% confidence level. Therefore, the standard deviation does not increase as the mean increases. This may indicate that the user site source is more reproducible than the manufacturer site source.

Analytical Results: DNPH-Coated Cartridge/HPLC Method

The results from the HPLC analysis of the DNPH-coated cartridge samples are presented in Table 4-6. No samples were spiked because, at the time of the sampling, no spiking procedure had been established. Testing of the data as described above revealed no level dependence for the cartridge data with a calculated t-value of 2.002.

Methods Comparison: DNPH Impinger/HPLC and DNPH-Coated Cartridge/HPLC

Before comparison could be made between the two methods, the Bartlett test was used to determine if the variances for each data set were homogeneous. The Bartlett test yielded Chi Squared values of 11.4 and 16.6 for the impinger and cartridge data sets, respectively, neither of which exceeded the critical value of 19.7, for 11 degrees of freedom and the 95% confidence level. Therefore, for each data set the variances were homogeneous and standard deviations could be calculated for the data set as a whole that were more representative of the data than the values calculated from any run. The respective, pooled standard deviations for the impinger and cartridge data were thus calculated to be 0.049 and 0.023 mg/m^3. Following this, the two data sets were compared with each other using analysis of variance for a two-way classification as shown in Table 4-7. The calculated F-value for the comparison of the two methods was 44.67, which exceeded the critical value, $F_{1,11}$ = 4.86 at the 95% confidence level. On the basis of this determination, a value of the average difference was calculated, 0.079 ± 0.011 mg/m^3. Thus, the DNPH cartridges produced demonstrably higher values, which varied between 4 and

TABLE 4-6. SITE B: FORMALDEHYDE USER FACILITY - DNPH-COATED CARTRIDGE RESULTS

Formaldehyde Concentration, mg/cubic m

Run No.	Manifold Position 1	2	3	4	Mean	Std. Dev.	%RSD
1	0.863	0.866	0.850	0.834	0.853	0.015	1.7
2	1.985	1.959	1.890	1.941	1.944	0.040	2.1
3	1.705	1.756	1.723	1.719	1.726	0.022	1.3
4	0.862	0.858	0.835	0.852	0.852	0.012	1.4
5	0.860	0.866	0.888	0.874	0.872	0.012	1.4
6	1.265	1.337	1.326	1.351	1.320	0.038	2.9
7	0.818	0.875	0.897	0.878	0.867	0.034	3.9
8	0.886	0.879	0.875	0.894	0.884	0.008	0.9
9	0.797	0.748	0.744	0.744	0.758	0.026	3.4
10	1.230	1.228	1.252	1.234	1.236	0.011	0.9
11	0.904	0.922	0.930	0.940	0.924	0.015	1.6
12	0.845	0.853	0.873	0.870	0.860	0.013	1.6

TABLE 4-7. FORMALDEHYDE SITE B DATA

TWO-WAY ANOVA

Run No.	DNPH Impingers	DNPH-Coated Cartridges
1	0.735	0.853
2	1.882	1.944
3	1.561	1.726
4	0.763	0.852
5	0.826	0.872
6	1.282	1.320
7	0.830	0.867
8	0.786	0.884
9	0.645	0.758
10	1.188	1.236
11	0.832	0.924
12	0.823	0.860

$\bar{x}$ = 1.05204

s^2 = 0.13795

Analyses of Variance

Source	Degrees Freedom	Sums of Squares	Mean Squares	F-value
METHOD	1	0.03705	0.03705	44.67*
RUN	11	3.26457	0.29678	357.78
ERROR	11	0.009124	0.0008295	
TOTAL	23	3.31075		

$F_{1,11}$ for 95% confidence level 4.86

Method Differences are significant

*Significant at 95% confidence level

12% in the present study. Again, there is no one, apparent explanation for the difference observed. Several parameters which collectively may have contributed to this difference include slightly lower collection efficiency in the impingers, loss from the impingers (in the form of aerosol), and some minor interferent or formaldehyde background on the cartridges.

SECTION 5
QUALITY CONTROL

GENERAL

Good laboratory practices were followed throughout the project. All glassware was cleaned carefully and reagent grade chemicals were used. Calibration curves for both the ion chromatograph and the high performance liquid chromatograph were prepared each day that samples were analyzed.

SAMPLE STABILITY

Peroxide Impinger Samples

Peroxide impinger samples were allowed to stand overnight and then analyzed as soon as possible. Laboratory experiments indicated that the formate peak grew larger with time for samples that were reanalyzed. Attempts to destroy the excess peroxide by gentle heating or by use of a catalyst were unsuccessful. The peroxide impinger/ion chromatography method needs further study before it can be recommended as an alternate method.

DNPH Impinger Samples and DNPH-Coated Cartridge Samples

Earlier laboratory experiments at RTI indicated that standards prepared in acidified DNPH were stable over a period of at least fifteen (15) days. Therefore, it was assumed that the DNPH impinger samples and the cartridge extracts would be stable. To check the stability of collected samples, selected samples covering a wide range of concentrations were reanalyzed after a period of 3 days, 7 days, or 11 days. The results are summarized in Table 5-1. All samples showed a slight increase in concentration.

ANALYTICAL RECOVERY

A test for analytical recovery from the field samples was conducted using the method of standard additions. In this procedure, selected impingers were spiked with accurately measured quantities of formaldehyde DNPH derivative or prior to addition of the collection solution. For each run, the mean of the unspiked sample values was subtracted from the measured value of the sample

TABLE 5-1. STABILITY DATA FOR DNPH IMPINGER AND CARTRIDGE SAMPLES

Sample ID	μg derivative/mL Analysis 1	Analysis 2	Percent Change in Concentration	Δ time, days
Impinger:				
A1-3	65.37	66.86	+2.28	7
A3-3	65.27	65.59	+0.49	7
A4-3	73.74	74.53	+1.07	7
A5-1F	10.44	10.98	+5.17	11
A6-3F	14.49	14.85	+2.48	11
A7-4F	15.99	16.56	+3.56	11
A8-2F	14.93	15.57	+4.29	11
B1-4F	2.47	2.54	+2.76	3
Cartridge:				
B1-2F	7.79	7.87	+1.02	3

containing the spike, and this difference was compared with the prepared value of the spike. In the Site A test, the comparisons were made with log-transformed values. These data, presented in Table 5-2, are not significantly different since the mean (0.027) of the paired differences was not significantly different from zero. That is, the recovered amounts were not statistically different at the 95% confidence level from the amounts spiked. The calculated t-value, 0.77, for the mean did not exceed the critical value of 2.571 for five degrees of freedom at the 95% confidence level. Neither was there a significant difference found when comparing the Site B spike values with the measured values as shown in Table 5-3. The mean difference was 0.038 with a standard deviation of 0.042, which resulted in a calculated t-value of 0.826 that was less than the critical value cited above. The average recoveries for Sites A and B were 98 and 92 percent, respectively, showing that recoveries for the methods are acceptable.

TABLE 5-2. ANALYTICAL RECOVERY RESULTS: SITE A

Run	Prepared Spike Value	Spiked Sample Measure	Unspiked Mean	Spike Measure	Transformed Spike Value	Transformed Spike Measurement	Difference
2-1	393.5	683.9	292.8	391.1	5.975	5.969	0.006
2-3	373.1	644.3	292.8	351.5	5.922	5.862	0.060
6-1	308.0	385.3	57.93	327.37	5.730	5.791	-0.061
8-4	347.9	364.7	69.63	295.07	5.852	5.687	0.165
9-3	89.2	802.1	713.8	88.3	4.491	4.428	0.062
11-4	307.0	1067.1	738.83	328.27	5.727	5.794	-0.067

Mean = 0.027

Standard Deviation = 0.036

t-statistic 0.77

t, v = 5, 2.571

TABLE 5-3. ANALYTICAL RECOVERY RESULTS. SITE B

Run	Prepared Spike Value	Spiked Sample Measurement	Unspiked Mean	Spike Measurement Difference	Deviation from Prepared Value Δ
1	0.260	0.983	0.735	0.248	0.012
3	0.269	1.745	1.561	0.184	0.085
6	1.053	2.346	1.282	1.064	-0.011
8	0.970	1.798	0.786	1.012	-0.042
10	1.086	2.049	1.188	0.861	0.225
12	1.046	1.910	0.823	1.087	-0.041
				Mean =	0.038
				Standard Deviation =	0.042
				t-statistic	0.826
				t, v = 5,	2.571

SECTION 6
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APPENDIX A

SUGGESTED OPERATING PROCEDURE FOR DETERMINATION OF FORMALDEHYDE EMISSIONS FROM STATIONARY SOURCES

SUGGESTED OPERATING PROCEDURE FOR DETERMINATION OF FORMALDEHYDE EMISSIONS FROM STATIONARY SOURCES

Formula: CH_2O

Molecular Weight: 30.026

1. PRINCIPLE

1.1 Principle. A gas sample is extracted from the effluent of the stack. The dissolved formaldehyde is reacted with 2,4-dinitrophenylhydrazine (DNPH) in the impinger solution and is measured as the hydrazone derivative using high performance liquid chromatography.

2. APPARATUS

2.1 Sampling. The sampling apparatus is shown in Figure 1. Component parts are described below:

2.1.1 Sampling Probe. Teflon tubing, 10 feet long, 1/4 inch OD, 3/16 inch ID. Each probe has a size 12/5 spherical glass socket joint on one end. The other end is packed with a small plug of silanized glass wool. It may be necessary to use a heated disk filter instead of a glass wool plug when sampling from sources containing high moisture levels. Any moisture on the glass wool plug will collect formaldehyde.

2.1.2 Impingers. Midget impingers, 25 mL capacity with size 12/5 spherical glass ball joints.

2.1.3 Sampling Pumps. Battery powered air sampling pump, SKC Model 222-3 or equivalent. Flow rate is adjustable between 50 and 200 mL per minute. Sample volume is determined from number of pump strokes accrued on counter.

2.1.4 Interconnections. Glass U-tube with size 12/5 spherical glass socket joints for connecting front and back impingers. Tygon tubing with a size 12/5 spherical glass socket joint on one end for connecting back-up impinger to sampling pump.

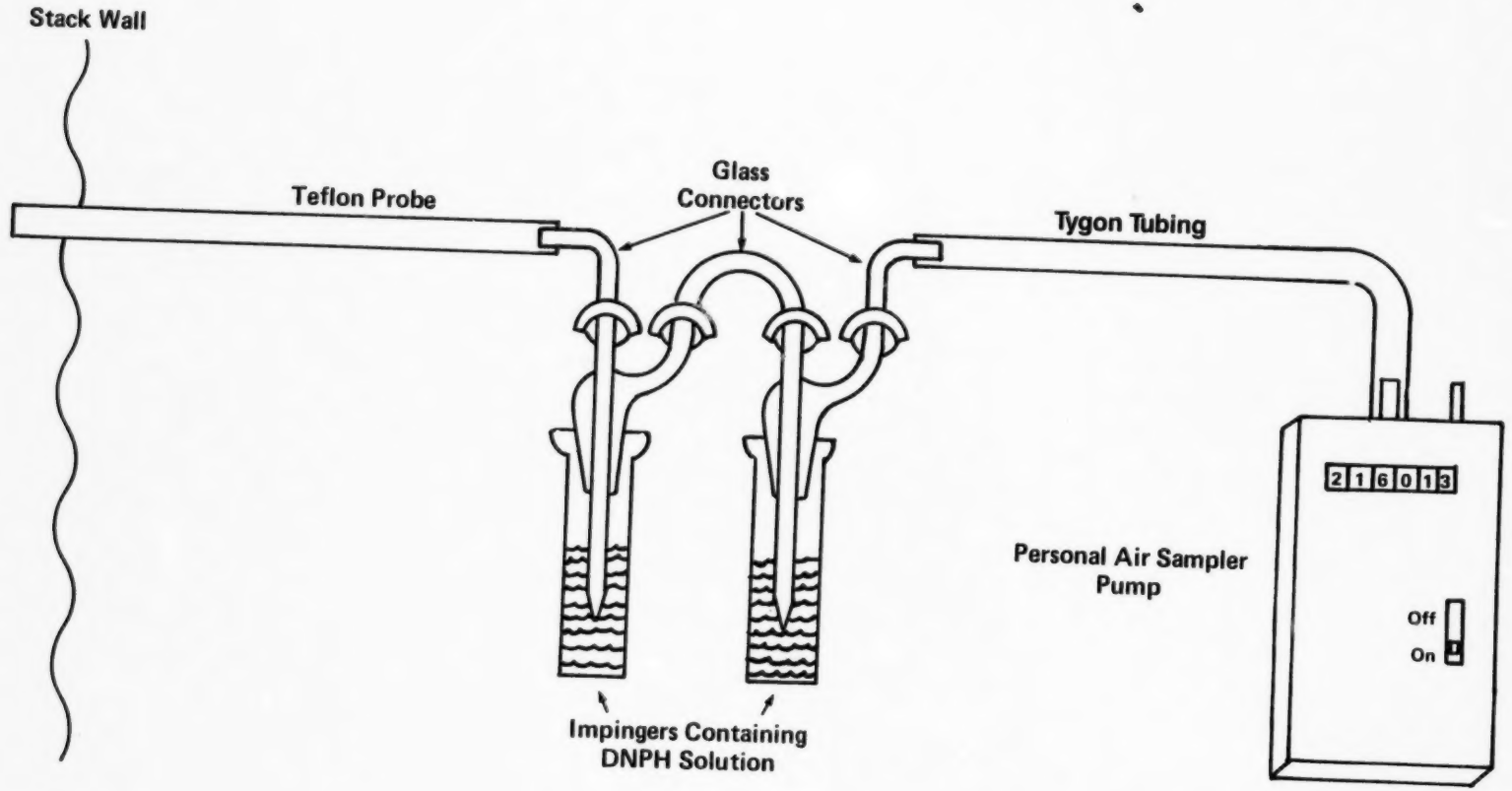

Figure 1. Formaldehyde sampling apparatus.

2.1.5 Thermometer. 0 - 50°C range for measuring ambient temperature.

2.1.6 Barometer. Aneroid barometer for measuring atmospheric pressure.

2.2 Sample Recovery.

2.2.1 Storage Vials. 50 mL capacity for transport of samples if impingers are to be reused in the field.

2.3 Sample Preparation.

2.3.1 Volumetric Flasks. Class A volumetric flasks, an assortment of sizes including 25 mL and 50 mL, for transfer and/or dilution of impinger samples.

2.3.2 Volumetric Pipets. Class A pipets, an assortment of sizes, for dilution of samples into the range of the calibration standards, if necessary.

2.4 Analysis.

2.4.1 Volumetric Flasks. Class A volumetric flasks, an assortment of sizes, for preparing calibration standards.

2.4.2 Volumetric Pipets. Class A pipets, an assortment of sizes, for preparing calibration standards.

2.4.3 Microsyringe. Appropriately sized syringe for injection of calibration standards and samples.

2.4.4 Liquid Chromatograph.

2.4.4.1 Sample Loop. Fixed volume, 20 μL.

2.4.4.2 Column. Zorbax-ODS column, 25 cm X 4.6 mm ID. Isocratic conditions with 65% acetonitrile and 35% water at a flow rate of 1 mL/min.

2.4.4.3 Detector. Variable wavelength detector set at 365 nm.

2.4.4.4 Integrator. Shimadzu C-R3A chromatopac, or equivalent, for quantitation by peak area integration.

3. REAGENTS

The highest purity reagents should be used, particularly in the preparation of calibration standards.

CAUTION: Care should be taken when using 2,4-dinitrophenylhydrazine (DNPH), acetonitrile (ACN), and perchloric acid. DNPH and ACN are flammable and are harmful if swallowed, inhaled, or absorbed through the skin. All three chemicals can be dangerous if handled improperly.

3.1 Sampling.

3.1.1 2,4-dinitrophenylhydrazine (Aldrich Chemical Co.). Recrystallized in HPLC grade ACN at 40 - 60°C by slow evaporation of the solvent.

3.1.2 Saturated DNPH Solution. Place purified crystals of DNPH in a 1-L glass bottle with a ground glass top. Add approximately 50 mL ACN to the bottle, agitate gently, and allow to stand overnight. Add ACN as necessary, taking care that a large excess of purified crystals remains in the bottom of the bottle. The saturated solution contains ~ 11 mg DNPH per mL at room temperature.

3.1.3 Acetonitrile. HPLC grade, for preparation of impinger solution.

3.1.4 Perchloric Acid, 3.8M. Prepared from reagent grade perchloric acid.

3.1.5 Impinger solution. Dilute 25 mL of saturated DNPH solution to 100 mL with ACN and acidify with 1.0 mL of 3.8M $HClO_4$.

3.2 Sample Recovery and Preparation.

3.2.1 Acetonitrile (ACN). HPLC grade, for quantitative transfer of impinger solutions and for sample dilution.

3.3 Analysis.

3.3.1 Formaldehyde-DNPH Derivative. Purified derivative prepared according to Section 4.4.2.1, for preparation of calibration standards.

3.3.2 Acetonitrile. HPLC grade, for use in the preparation of calibration standards. Also used to prepare the HPLC eluent.

3.3.3 Deionized Water. For used in the preparation of the HPLC eluent.

4. PROCEDURE

4.1 Sampling.

4.1.1 Preparation. Secure end of probe with glass wool plug in duct or stack port with the probe tip near the center of the source gas stream. Fill two impingers with 20 mL each of DNPH/acetonitrile sampling media. Connect probe outlet to sampling pump inlet tube using a glass union with size 12/5 spherical glass ball joints. Start sampling pump and allow sample probe to purge for 5 minutes (if a longer probe is used, increase purge time proportionally). After purging is complete, stop pump, attach probe to the front impinger, connect front impinger to back-up impinger, and connect back-up impinger to the sampling pump.

4.1.2 Sample Collection. Record the ambient temperature and pressure. Record the initial pump counter reading, start the sample pump, and begin timing. After an appropriate period of time, stop pump and record final pump counter reading. One hour of sampling has been found to be appropriate for formaldehyde manufacturer and user sites. Sampling from incinerators will probably require two hours to achieve measurable levels. Appropriate sampling times should be determined from analysis of samples collected during the pretest survey.

4.1.3 Sample Recovery. Disconnect impingers and seal inlet and outlet joints with Parafilm. If impingers must be reused, transfer contents to separate storage vials along with several rinses of acetonitrile. Store sample solutions on ice for transport to the laboratory.

4.2 Sample Preparation. Quantitatively transfer the solutions from the front and back impingers into separate 25 mL volumetric flasks and dilute each to the mark with ACN. Analyze the solutions to determine whether significant breakthrough has occurred, e.g., >10 percent. When it has been determined that there is no significant breakthrough of formaldehyde into the back impinger, the front and back impingers may be combined for a single analysis for subsequent runs. If the

concentration of formaldehyde is near the low end of the calibration curve, combination of the impingers may dilute the sample to an unquantifiable concentration. In this case, it is acceptable to analyze only the front impinger from each pair after it has been demonstrated that there is no breakthrough. If the source emission rate is known or suspected to be quite variable, samples should be checked periodically for significant breakthrough.

4.3 Sample Analysis. Using the 20 μL fixed-volume sample loop, inject duplicate aliquots of each sample into a calibrated liquid chromatograph. The concentrations of the calibration standards should bracket the range of concentrations found in the samples. Plot the chromatograms and collect the integration data for later analysis.

4.4 Calibration.

4.4.1 Pump. Fully charge pump batteries prior to calibration. Fill two sampling impingers with 20 mL of acetonitrile each and attach impingers to sampling pump as for source sampling. Attach a soap-film flowmeter to the front impinger inlet. Start pump and adjust the flow rate based on the source concentration anticipated. After adjustment, measure the flow rate three times and average. Measure the pump stroke rate by timing the pump counter for 100 counts, averaging the results of 3 measurements. Divide the average flow rate (mL/minute) by the average stroke rate (counts/minute) to calculate the pump factor (mL/count). Apply this factor to the counts accumulated during sampling to determine the sample volume.

4.4.2 Gas Chromatograph. A multilevel calibration of the HPLC is performed using a series of solutions of the formaldehyde-DNPH derivative at known concentrations.

4.4.2.1 Preparation of Formaldehyde-DNPH Derivative. Titrate a saturated solution of purified DNPH in 2N HCl with formaldehyde. Filter the bright yellow precipitate and wash with 2N HCl followed by deionized water.

Allow to air dry. Check the purity of the derivative by melting point determination. If necessary, recrystallize from absolute ethanol or methanol.

4.4.2.2 Preparation of Standards. Prepare a stock solution of the formaldehyde-DNPH derivative by transferring an accurately weighed quantity of the derivative to a volumetric flask and diluting the the mark with ACN. By dilution of the stock solution, prepare at least three levels of calibration standards that bracket the range of concentrations expected to be found for the samples. Calibration standard concentrations and sample concentrations are calculated as μg formaldehyde-DNPH derivative per mL.

5. CALCULATIONS

5.1 Field Data. Calculate the number of moles of air sampled:

$$n_1 = \frac{P_A V}{P_S T_A R}$$

where: n_1 = number of moles of air sampled

V = volume of air sampled, liters

P_S = standard pressure, 760 mm Hg

P_A = average ambient pressure during sample collection, mm Hg

T_A = average ambient temperature during sample collection, °K

R = gas constant, 0.08206 L atm/°K mol

5.2 Laboratory Data. Calculate the number of moles of formaldehyde collected.

$$n_2 = \frac{C_S V_S}{M.W_D} \times DF \times 10^{-6}$$

where: n_2 = number of moles of formaldehyde collected

C_S = sample concentration, μg derivative/mL

V_S = sample volume, mL

DF = dilution factor (= 1 if samples were not diluted)

$M.W_D$ = gram molecular weight of formaldehyde-DNPH derivative, 210.149 g/mole

5.3 Source Concentration. Calculate the formaldehyde source concentration:

$$C_S = (n_2/n_1)\ 10^6$$

where: C_S = formaldehyde source concentration, ppm

5.4 Statistical Treatment. The data for each sample set is used to determine the precision of the method by calculating the relative standard deviation of the measurements within that particular sample set:

$$\%\ RSD = (s/x)\ 100$$

where: RSD = relative standard deviation of sample set results

s = standard deviation of sample set data

x = average concentration of sample set